IOP Conference Series: Materials Science and Engineering

PAPER • OPEN ACCESS

Utilization of Emission Carbon Dioxide Gas into High Economic Value Chemicals: Diethyl Carbonate

To cite this article: D Aslya *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **543** 012071

IOP Conf. Series: Materials Science and Engineering **543** (2019) 012071 doi:10.1088/1757-899X/543/1/012071

Utilization of Emission Carbon Dioxide Gas into High Economic Value Chemicals: Diethyl Carbonate

D Aslya[1], S Febriani[1], F Adian[1], R Tetrisyanda[2], A Wiguno[2], S Gunawan[2], F Kurniawansyah[2] and G Wibawa[2,*]

[1] Research Technology Center, PT. Pertamina (Persero), Jakarta, 13920, Indonesia
[2] Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Surabaya, 60111,Indonesia

*Email: gwibawa@chem-eng.its.ac.id

Abstract. Utilizing fossil fuel is always has a deficiency in the environmental aspect. The processing of fossil fuel produce high carbon dioxide (CO_2) emissions. It is required an effort to utilize CO_2 emissions into feed of a high-economic value product of such as diethyl carbonate (DEC). The objective of this study was to develop the process of DEC synthesis from CO_2 using ethanol and ethylene oxide as reactant and potassium iodide – based catalyst. The catalyst used in the experiment were binary catalyst potassium iodide (KI) – cerium oxide (CeO_2) and KI – sodium ethoxide (EtoNa). The experiment conducted in cylindrical reactor equipped with stirrer and heating jacket. Reactant and catalyst were added into reactor and setting operation condition at initial pressure of 35 bar and temperature of 170 °C within 3 hours. The ratio of ethylene oxide to ethanol was investigated as well. Subsequently, the products of this synthesis were analyzed qualitatively and quantitatively to determine the reaction products and DEC yield. From the experiment, DEC was successfully obtained and the highest DEC yield was found to be 7.1 % by using KI-EtoNa as catalyst at mole ratio of ethylene oxide to ethanol of 1:15 within 3 hours of reaction time.

1. Introduction

Fossil-based energy sources (petroleum, natural gas and coal) are the main energy sources used by most of the Indonesian people. In its development, consumption of fossil-based energy sources will increase in the next few years. However, fossil-based energy resources are known as the main carbon emitters. Currently the petroleum, natural gas and coal industries have real responsibilities and challenges in meeting future energy needs by facing environmental impacts and issues.

The utilization of carbon dioxide as the main raw material in the process of making an economic value product is an alternative process that can be applied to reduce gas emissions from the processing and utilization of fossil-based energy. Carbon dioxide (CO_2) emissions not generated only from fuel production but also from mobiles vehicles contribute to global warming [1]. The addition of additives such as ethanol to the fuel becomes an important aspect given by the increasing levels of pollution in the environment. Ethanol is renewable energy which can be obtained from lignocellulosic materials [2]. However, the use of ethanol has the disadvantage of increasing the vapour pressure of gasoline [3-4].

The use of ethanol as an additive in a mixture of fuels besides having high RON (table 1) is also based on its non-toxic properties and abundant availability of biomass. However, the use of ethanol has the disadvantage of being able to increase vapor pressure gasoline [5]. The addition of ethanol to the isoocatane (the main component of gasoline) increases the pressure of the gasoline mixture. This increase in vapor pressure causes the gasoline mixture emissions to increase. In addition to this, the property of ethanol which is hygroscopic causes water to dissolve in gasoline to increase so that the quality of gasoline decreases [6]. So that additional additives are needed to overcome the problem. These additional additives are not expected to also have characteristics that can improve combustion performance.

Table 1. The octane value of various additives.

Additive	RON
Methyl tert-butyl ether	105-123
Ethanol	120-135
Diethyl carbonate	111
Dimethyl carbonate	101

One product that can be produced using carbon dioxide is diethyl carbonate (DEC). DEC can be used as an additive in diesel and gasoline fuel to reduce pollutant emissions because DEC has a high oxygen content [7-8]. The addition of DEC in alcohol-gasoline blends can reduce the mixtures vapour pressure [9-10]). The use of carbon dioxide emission gas into DEC is a very effective and efficient alternative in tackling emissions in the environment by integrating DEC production units with CO_2 emitting units.

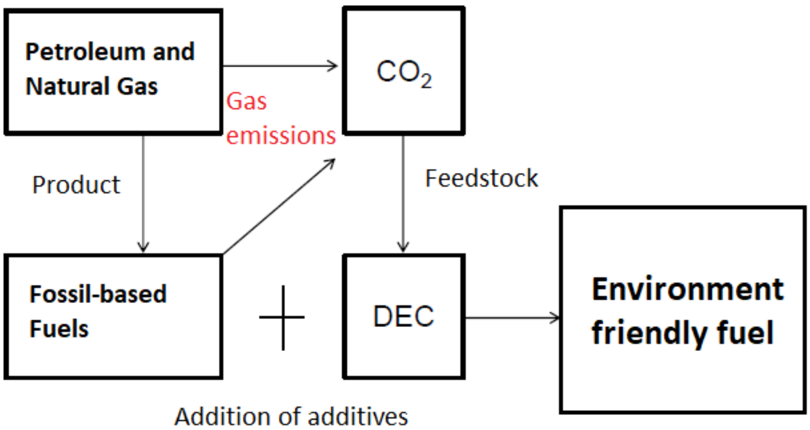

Figure 1. Integration scheme of gas emission utilization from the energy industry.

From the explanation above, the need for an environmentally friendly energy industry can be realized if there is integration between the energy producing industry and the emission gas utilization unit as shown in figure 1. Gas emissions produced from processing oil and natural gas are captured to become raw material for DEC production. After that, the use of fossil-based fuel products formed will also produce dangerous gas emissions. So adding DEC not only makes burning fuel more perfect but also makes the energy industry more environmentally friendly.

The method of synthesis of DEC has been developing for a long time. Some synthesis routes are the phosgene-ethanol method, DEC formation of ethanol into ethyl nitrite [11], oxidative carbonylation of ethanol [12], gas-phase oxidative carbonylation of alcohol [13] and activation of CO_2 [14]. DEC synthesis using carbon dioxide has been developed by many studies. The formation of DEC is done by reacting carbon dioxide with ethanol, which will produce DEC and water [15]. In the synthesis reaction of DEC through one pot reaction with ethanol and CO_2 reactants, the following equation is shown in equation (1).

$$\textit{Ethanol} + \textit{Carbon Dioxide} \rightarrow \textit{Diethyl Carbonate} + \textit{Water} \quad (1)$$

In general, the DEC synthesis reaction requires dehydration agents to shift equilibrium towards DEC products. Therefore, ethylene oxide is needed to increase DEC production. The reaction mechanism of DEC synthesis from carbon dioxide using ethylene oxide was proposed by previous work [16]. The catalyst was very influential on the DEC formation process. Therefore, the aim of this work is to develop DEC synthesis technology using heterogeneous and homogeneous catalysts. In addition, the effect of using the mole ratio of reactants between ethanol and ethylene oxide was also studied in this work.

2. Experimental Section

2.1. Description of Materials

The materials used in this work were carbon dioxide, ethanol, and ethylene oxide as reactants. Ethanol were used using further purified by molecular sieve to remove the water contaminant and other materials were used without further purification. The reactant specifications are given in table 2. The binary catalyst of potassium iodide (KI) and cerium oxide (CeO2) or sodium ethoxide (EtoNa) were used in the DEC synthesis. The binary catalyst mass ratio was 1:3.

Table 2. Properties and specifications of reactant.

Component	Source	Purity (%)	Molecular Weight ($g.mol^{-1}$)
Carbon dioxide	Samator, Indonesia	99.8	44.01
Ethanol	Merck, Germany	99.5	46.07
Ethylene oxide	Aneka Gas, Indonesia	90	44.05

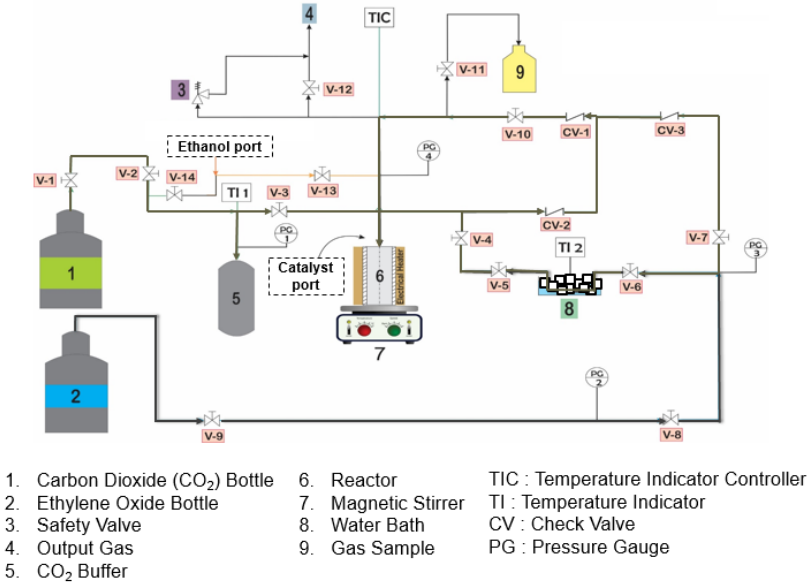

Figure 2. Experimental apparatus.

2.2. Experimental Procedures

The synthesis of DEC was conducted in 345 ml cylindrical stainless steel reactor equipped with stirrer and heating jacket. The reactor is also equipped with thermocouples and pressure indicators. Pressure control were done manually through a valve connected to the reactor. Thermocouples was used to monitor and control the temperature of the reactor using the TC-4S Autonic. The experimental apparatus was shown in figure 2.

The study was started by weighing ethanol and catalyst on the OHAUS analytic balance with an accuracy of ± 0.0001 grams. The experiment was carried out by mixing ethanol with 0.2 gram of catalyst into the reactor and ensure no air contamination in the reactor. After that, inject 0.023 mole ethylene oxide into the reactor and followed by CO2 up to initial pressure 30 bar. The operating conditions at the reactor was kept constant at 443K during the reaction time. The mole ratio between ethylene oxide and ethanol was studied between 1:5, 1:10 and 1:15 and the reaction time was 3 hours. After the specified time, the reactor temperature was reduced to room temperature then the pressure on the reactor was slowly released to the air by release valve. The liquid phase product is separated from its solid catalyst and analysed for DEC yield in the product by using gas chromatography.

3. Results and Discussion

Synthesis of diethyl carbonate (DEC) was carried out by reacting CO_2, ethanol with ethylene oxide using KI –CeO_2 and KI – EtoNa catalysts. From the GC-MS qualitative analysis it is shown that DEC synthesis has been successfully demonstrated in the three reactions that occur in accordance with the reference where four compounds were formed in this synthesis, including 2-ethoxyethanol, ethylene glycol, diethyl carbonate, and ethylene carbonate. The catalytic mechanism produces the reaction of ethylene oxide (EO) and CO_2 in the first cycle which occurs to form ethylene carbonate (EC) through the cycloaddition reaction following equation (2). At this step, the reaction runs very effectively. For the second cycle, EC transesterification with ethanol occurs to produce DEC and Ethylene glycol (EG) according to equation (3). Side reactions that occur are 2-ethoxyethanol formation from EO and ethanol reactants following equation (4).

Ethylene Oxide + Carbon Dioxide → Ethylene Carbonate (2)

Ethylene Carbonate + Ethanol → Diethyl Carbonate + Ethylene Glycol (3)

Ethylene Oxide + Ethanol → 2-ethoxyethanol (4)

The results of the quantitative analysis of each experiment are shown in table 3. DEC yield is a percentage of the number of DEC moles formed on the number of moles of ethylene oxide used in the reactor.

Table 3. DEC synthesis results using KI – CeO2 catalyst.

Catalyst	Ethylene oxide : Ethanol (Mole ratio)	DEC Yield (%)
KI – CeO_2	1:5	0.365
	1:10	1.064
	1:15	1.109
KI - EtoNa	1:5	2.158
	1:10	2.54
	1:15	7.097

Catalyst is very important parameter in DEC synthesis. The effect of homogen and heterogen catalyst was observed in this study. From figure 3, it is shown that the homogen catalyst KI – EtoNa give better DEC yield than heterogen catalyst KI – CeO_2. KI catalyst has an important role in the cycloaddition reaction and sodium ethoxide has an important role in the transesterification reaction. The mechanism of transesterification with ethanol and ethylene carbonate catalysed by sodium ethoxide is a classic addition-elimination process (Zhang et al., 2014). KI and EtoNa are homogeneous catalysts, which are soluble in ethanol, so that the catalyst can more effective in DEC formation. Thus, the homogeneous catalyst is superior in terms of activity and selectivity. Moreover, EtoNa is a base type catalyst which suitable for the reaction of DEC synthesis. CeO_2 catalyst is a heterogeneous catalyst that does not dissolve in ethanol, so that small active surface can come into contact with the reactants during the reaction. However, this heterogeneous catalyst is superior in terms of separation from the product mixture [17].

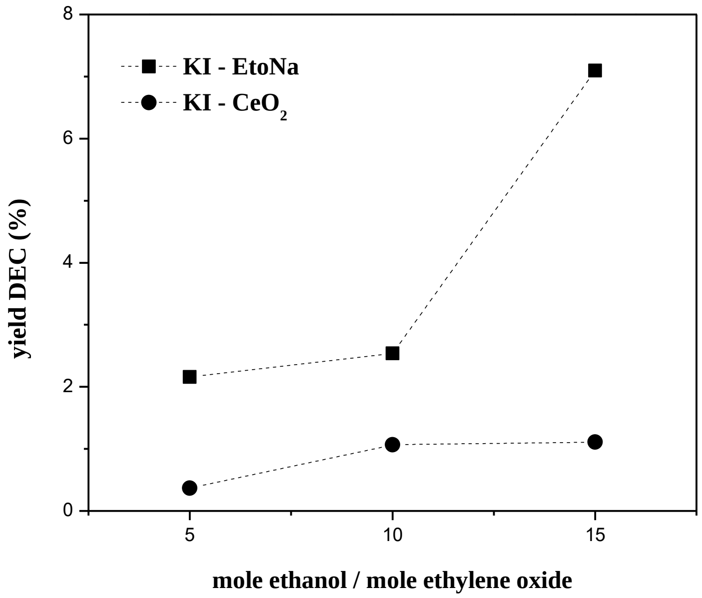

Figure 3. Effect of ethanol to ethylene oxide mole ration on DEC yield.

In DEC synthesis, dehydrating agent is one of the important compounds to be used. Ethylene oxide was used as dehydrating agent by removing thermodynamic limitations by shifting equilibrium towards the carbonate production. From figure 3, it shown that with the increasing ratio of ethanol to the ethylene oxide, the number of DEC compounds formed significantly increases with the best mole ratio 1:15. In this synthesis, ethanol is an excess reactant. With the increase in the mole ratio between ethanol and ethylene oxide it will also have an impact on the mole ratio between H_2O and ethylene oxide, which will increase the rate of hydrolysis reaction of the ethylene oxide itself, so that there will be a reaction that rivals the main reaction in DEC synthesis.

4. Conclusions

Environmental emission gas carbon dioxide has potential to be used as feed material in the process diethyl carbonate sythesis. Diethyl carbonate has high economic value and it can be used as gasoline additives. This potential can be used as an alternative to mitigate the gas emission waste of the energy industry so that it can become more environmentally friendly industry. From the results of this study, it was found that the processing of carbon dioxide to diethyl carbonate produced the best yield of 7.1% using homogeneous KI-EtoNa catalyst as catalyst at mole ratio of ethylene oxide to ethanol of 1:15 within 3 hours of reaction time. The use of homogeneous catalysts is superior to heterogeneous catalyst.

5. References

[1] Hanpattanakit P, Pimonsree L, Jamnongchob A and Boonpoke A. 2018 *Chem. Eng. Trans.* **63** 37-42
[2] Da Silva A R G, Errico M and Rong B G 2017 *Chem. Eng. Trans.* **57** 1-6

[3] Oktavian R, Amidelsi V, Rasmito A and Wibawa G 2013 *Fuel* **107** 47-51
[4] Anugraha R P, Altway A and Wibawa G 2017 *J. Chem. Eng. Data* **62** 2362-66
[5] Aulich T R, He X, Grisanti A A and Knudson C L 1994 *J. Air Waste Manag. Assoc.* **44** 1004-09
[6] Peng C, Lewis K C and Stein F P 1996 *Fluid Phase Equilibr.* **116** 437-44
[7] Pacheco M A and Marshall C L 1997 *Energy Fuels* **11** 2-29
[8] Dunn B C, Guenneau C, Hilton S A, Pahnke J and Eyring E M 2002 *Energy Fuels* **16** 177-81
[9] Anugraha R P, Picunang Z A A, Wiguno A, Tetrisyanda R, Kuswandi K and Wibawa G 2017 *Indones. J. Chem.***17** 500-8
[10] Anugraha R P, Wiguno A, Altway A and Wibawa G 2018 *J. Mol. Liq.* **264** 32-7
[11] Matsuzaki T and Nakamura A 1997 *Catal. Surv. Asia* **1** 77-88
[12] Zhang Z, Ma X, Zhang J, He F and Wang S 2005 *J. Mol. Catal A-Chem.* **221** 141-6
[13] Yanji W, Xinqiang Z, Baoguo Y, Bingchang Z and Jinsheng C 1998 *Appl. Catal. A Gen.* **171** 255-60
[14] Tomishige K, Sakaihori T, Ikeda Y and Fujimoto K 1999 *Catal. Lett.* **58** 225-9
[15] Leino E, Maki-Arvela P, Eranen K, Tehno M, Murzin D Y, Salmi T and Mikkola J P 2011 *Chem. Eng. J.* **176-177** 124-133
[16] Wang L, Li H, Xin S, He P, Cao Y, Li F and Hou X 2014 *Appl. Catal. A Gen.* **471** 19-27
[17] Van Klink G P M, Dijkstra H P and Van Koten G 2003 *C. R. Chim.* **6** 1079-85